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ION-MOLECULE CHEMISTRY RELATED TO
PLASMA DEPOSITION AND ETCHING OF SILICON

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During the 5 years of this contract, we used guided ion beam tandem mass spectrometric methods to study a variety of gas-phase ion-molecule reactions relevant to plasma deposition and etching of silicon. Absolute cross sections over a wide range of kinetic energies for reactions involving both atomic and polyatomic ions were measured. The results yielded energy dependent cross sections, temperature dependent rate constants, and thermochemical data, information vital to further understanding of the chemical mechanisms involved in plasma processing.

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1. Project Description

The results of the work performed in our laboratory during the course of this contract have been disseminated in 20 published papers,[1-20] and 2 papers submitted for publication.[21,22] In addition, 6 invited seminars and 4 contributed papers concerning Air Force supported work have been presented by the PI or members of my group. The work falls into several categories and is summarized below.

A. Introduction and Background

An important tool in the fabrication of microelectronic devices is the use of plasmas to etch and deposit silicon, silicon oxide, silicon carbide, silicon nitride, and other semiconductor material layers. During etching, highly reactive radicals and ions present in the plasma bombard the surface and volatilize the silicon, silicon dioxide, silicon nitride, or other components of the surface. Deposition of silicon dielectric films involves polymerization of silicon-containing radicals and ions. The role of gas-phase ion-molecule reactions in these processes is as yet unclear. Although radical-molecule reactions dominate the chemistry at the surface, gas-phase ion-molecule reactions are a substantial source of neutral radicals that can rival their production via electron-impact dissociation.[23,24] Therefore, the role of ion-molecule reactions in plasma processing deserves further investigation, and must be included in accurate modeling of the plasma environment.[25] In the past, such modeling was often forced to assume that the ion-molecule reactions are independent of collision energy, an assumption that we have subsequently shown is often invalid.[3,6,10,12] Accurate modeling of these systems requires cross sections or rate constants as a function of energy up to at least 40 eV, information provided in our work.

During the course of the contract, we studied a number of ion-molecule reactions related to plasma deposition and etching of silicon. Our studies examine these reactions over a broad range of kinetic energies by using guided ion-beam mass spectrometry. The

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basic information provided is absolute reaction cross sections as a function of kinetic energy. In most studies, this information is interpreted to determine mechanisms of the reactions and relevant thermochemistry of the reactive ionic and neutral species of potential importance in plasma environments. Such thermodynamic information is a critical tool in understanding deposition and etching processes and in evaluating the optimum conditions for plasma reactors.[26]

B.   Experimental Methods

General. The experimental technique used throughout these studies was guided ion beam tandem mass spectrometry.[27] In this instrument, ions are produced by one of several techniques described below. The ions are then focused into a beam, mass analyzed, and decelerated to a desired kinetic energy. The ion beam is injected into an rf octopole beam guide,[28] which acts as an ion trap. This ensures efficient collection of product ions and allows low energy (thermal) ion beams to be studied. The octopole passes through a reaction cell containing a neutral reactant gas maintained at sufficiently low pressure to ensure single-collision conditions. The product and unreacted ions drift out of the gas chamber to the end of the octopole where they are focused into a quadrupole mass filter for mass separation and detected by using a secondary electron scintillation detector and standard ion pulse counting techniques. Data collection is under computer control, which allows extensive signal averaging. The instrument incorporates extensive differential pumping that allows precise control over the conditions in the critically important reaction region.

Laboratory (lab) ion energies are converted to energies in the center-of-mass (CM) frame, the actual energy available for reaction. At each CM energy, E, the intensities of transmitted reactant and product ions are converted to absolute reaction cross sections for each product channel, $\sigma(E)$.[27] These cross sections have absolute uncertainties of ±20% up

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to ±50% for some charge transfer reactions. Relative cross section values are accurate to about ±5%. By using methods described elsewhere,[29] the thermodynamic thresholds of endothermic processes can be determined. We have demonstrated that these methods can provide accurate thermochemistry on a variety of transient species. Many of the studies summarized below are examples.

Ion Sources. In our work, ions may be generated by using several types of ion sources. This versatility permits the production of atomic and polyatomic ions with controlled internal excitation. This is important for two reasons. First, ions produced in a plasma environment have varying degrees of vibrational and/or electronic excitation. It has been shown previously in our laboratory that such excitation can have a significant effect on reactivity.[8,9,30] This effect can be studied explicitly by examining the reactions of ions generated under plasma-like conditions and those of ions with controlled internal excitation. The resulting state-specific cross sections and reactivity will be most useful in understanding and modeling the chemical and physical processes involved in the plasma systems of interest here. Second, accurate derivation of thermochemistry from the kinetic energy dependence of the reaction cross sections *requires* ions with well-characterized internal energies. This is most easily achieved by creating ions in their vibrational and electronic ground states.

Electron Impact Source. One method of ion production used in these studies is the standard electron impact (EI) source with variable electron energy. This source produces ions having a distribution of internal states, such that higher electron energies increase the probability of producing electronically excited ions. Only for ions with no low-lying excited states such as the rare gas ions can a ground electronic state beam be produced with the EI source.

Surface Ionization Source. In the surface ionization (SI) source, a filament is resistively heated and exposed to the parent gas resulting in decomposition and ionization.

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The ions are assumed to equilibrate at the filament with electronic state populations well-characterized by a Maxwell-Boltzmann distribution. The validity of this assumption has been discussed in the literature[31] and has recently been confirmed by van Koppen, et al.[32]

C.   Ion source development

Because of the importance of controlling the internal energy of the ions, one component of the contract work was to develop an ion source capable of producing polyatomic ions at a controlled temperature. The use of flow tube technology was used to accomplish this and our flow tube ion source is described in a paper supported by the Air Force.[11] Our flow tube can be varied in length (25, 50, 75 or 100 cm) and is pumped by a 600 cfm roots blower. The flow tube is followed by a 13-cm-long region that is held to about 10^{-4} Torr by an unbaffled 6" diffusion pump. Ion lenses in this region have an open construction in order to maximize pumping speed. Ions exit through an aperture into the first chamber of the guided ion beam apparatus (held below 10^{-6} Torr by a baffled 6" diffusion pump).

For a flow tube that is 1 m in length, the ions undergo $\sim 10^5$ collisions with the carrier gas (typically He or Ar) at a pressure of ~ 0.5 Torr. For the internal modes of polyatomic ions, Lineberger and coworkers have shown that these collisions serve to thermalize the ions, at worst to 1000 K, but more typically to 300 K.[33] Some limitations on the degree of collisional cooling do exist. For vibrational excitation, Ferguson has shown that vibrational quenching of small diatomic ions is very inefficient in He.[34] The use of argon as a bath gas or the addition of a more efficient quencher to the flow can alleviate such problems. For example, we have shown that we can effectively quench excited vibrational states of O_2^+ and N_2^+.[8,35] Our data for the covalently bound species, SiF_n^+ ($n = 1 - 4$)[20] and SF_n^+ ($n = 1 - 5$),[17] are consistent with thermalized ions, and studies of more weakly bound species, such as N_4^+,[11,15] $Fe(CO)_n^+$ ($n = 1 - 5$),[36] $Cr(CO)_n^+$ ($n = 1 - 6$),[37] and $H_3O^+(H_2O)_n$

$(n = 1 - 5)$[38] have shown that the internal energy of these ions is well described by a Maxwell-Boltzmann distribution of rotational and vibrational states corresponding to 298 K.

D. Silane chemistry

To complement earlier work on the reactions of Si^+ with silane, we performed two studies of the reactions of silane with various ions. In the first, the dissociative charge transfer reactions of silane with the rare gas ions (He^+, Ne^+, Ar^+, Kr^+, and Xe^+) was studied.[6] State-specific data for the $^2P_{3/2}$ ground spin-orbit states of Kr^+ and Xe^+ were included. The products observed in the He, Ar, and Kr systems are SiH_n^+ ($n = 0 - 3$). For the Ne system, formation of SiH_n^+ ($n = 0 - 2$) is seen, while in the Xe system only SiH_3^+ and SiH_2^+ are observed. Reactions of He^+, Ne^+, Kr^+, and Xe^+ show little dependence on kinetic energy, but for the case of Ar^+, the reaction probability and the product distribution are highly sensitive to the kinetic energy of the system. The results for these reactions were explained in terms of vertical ionization from the $1t_2$ and $3a_1$ bands of SiH_4. Thermal reaction rates were also provided and discussed.

The second study was published in a special issue of Z. Phys. D on "Collision Processes Relevant to Low Temperature Plasmas."[18] Here, we examined the reactions of SiH_4 with $O^+(^4S)$, $O_2^+(^2\Pi_g$, $v = 0)$, $N^+(^3P)$, and $N_2^+(^2\Sigma_g^+$, $v = 0)$. All four ions react with silane by dissociative charge-transfer to form SiH_n^+ ($n = 0 - 3$), and all but N_2^+ also form $SiXH_n^+$ products where ($n = 0 - 3$) and $X = O$, O_2 or N. The overall reactivity of the O^+, O_2^+, and N^+ systems show little dependence on kinetic energy, but for the case of N_2^+, the reaction probability and product distribution relies heavily on the kinetic energy of the system. These results can be understood by comparison with the rare gas ion study[6] and were again explained in terms of vertical ionization from the $1t_2$ and $3a_1$ bands of SiH_4. Thermal reaction rates were also provided and discussed.

E.   Silicon tetrafluoride chemistry

Building on an earlier study of the reaction of Si^+ with SiF_4,[39] we also studied the reactions of SiF_4 with He^+, Ne^+, Ar^+,[1] with O^+ and O_2^+,[9] and with $N^+(^3P)$, $N_2^+(^2\Sigma_g^+)$, $Ar^+(^2P_{3/2,1/2})$, and $Kr^+(^2P_{3/2})$.[19] In the first of these studies, dissociative charge transfer reactions are the sole processes observed. All SiF_n^+ ($n = 0$ - 4) products are observed, except for SiF_4^+ from reaction with Ne^+ and He^+, and Si^+ from reaction with Ar^+. At high energies, the dominant products are SiF_3^+ in the Ar system, and SiF^+ in both the Ne and He systems. There is some evidence in the Ne system for an excited state of SiF_3^+ at 5.7 eV. In the Ar^+ and Ne^+ reactions, the observed energetics are consistent with literature thermochemistry, but with He^+, reaction barriers are observed. The observed product distributions and energetics were explained by consideration of the potential energy surfaces and the difference in ionization energies of the rare gases.

In the second study,[9] the major reactions are again dissociative charge transfer processes, although O^+ also reacts to form $OF + SiF_3^+$ efficiently and O_2^+ reacts to form minor amounts of $SiOF_n^+$ ($n = 1$ - 3). Reactions of excited O_2^+ ions with SiF_4 are more efficient than reactions of ground state ions. Our work[19] on the reactions of $N^+(^3P)$, $N_2^+(^2\Sigma_g^+)$, $Ar^+(^2P_{3/2,1/2})$ and $Kr^+(^2P_{3/2})$ with SiF_4 was designed primarily to determine the thermochemistry for SiF_4^+ and SiF_3^+ more accurately. From the O^+ and N^+ systems, the adiabatic ionization energy, IE, of SiF_4 is 15.29 ± 0.08 eV, consistent with less precise determinations in the literature. The heat of formation of SiF_3^+ at 0 K is determined as -29.3 ± 0.6 kcal/mol, and that for NF as 63.4 ± 3.9 kcal/mol.

This thermochemistry was a necessary foundation to the follow-up study on the collision-induced dissociation (CID) and charge transfer reactions of SiF_n^+ ($n = 1$ - 4).[20] Energy dependences of the CID cross sections were analyzed to yield the following 0 K bond dissociation energies (BDEs): $D(SiF_3^+\text{-}F) = 0.85 \pm 0.16$ eV, $D(SiF_2^+\text{-}F) = 6.29 \pm 0.10$ eV, $D(SiF^+\text{-}F) = 3.18 \pm 0.04$ eV, and $D(Si^+\text{-}F) = 7.04 \pm 0.06$ eV. The ionization energies,

$IE(SiF_2) = 10.84 \pm 0.13$ eV and $IE(SiF_3) = 9.03 \pm 0.05$ eV, were also measured from analysis of endothermic charge transfer reactions. Combined with two other studies in our laboratories,[19,39] these results allowed us to derive heats of formation for the silicon fluoride cations and neutrals, Table I, that provide a self-consistent set of thermochemical data for the silicon fluoride species. In some cases, the thermochemical values determined here are considerably different from available literature values but are in good agreement with theory.[40,41,42,43]

Finally, in a study now ready for submission, we have examined the reactions of SiF_n^+ ($n = 1 - 3$) with SiF_4.[21] Absolute cross sections are measured as a function of kinetic energy from thermal to 20 eV. Transfer of F and F^- between the neutral and ion reactant are the major reaction channels and are distinguished by silicon isotope labeling. For all systems investigated, transfer of F^- is the dominant channel. Also observed is simple collision-induced dissociation of the reactant ions by sequential loss of fluorine atoms. The isothermal F^--transfer reaction of SiF_3^+ with SiF_4 exhibits an activation barrier of 0.29 ± 0.03 eV. All the reactions may be rationalized by collision-induced dissociation or attack on a F atom of SiF_4 by the Si atom of the ionic reactant. The propensities for F vs F^- atom transfer are rationalized in terms of molecular orbital correlations.

F.   Silicon tetrachloride chemistry

Our work on silicon tetrachloride involves three studies. In the first, the reaction of Si^+ with $SiCl_4$ was studied.[2] Exothermic production of $SiCl^+ + SiCl_3$ is the dominant process occurring on nearly every collision. $SiCl_3^+ + SiCl$ and $SiCl_2^+ + SiCl_2$ production are both found to be slightly endothermic, and the dissociative channels, $SiCl^+ + Cl + SiCl_2$ and $SiCl_2^+ + Cl + SiCl$, are also observed, but no $Si_2Cl_n^+$ species are observed. Isotopic labeling studies indicate that $SiCl^+$ and $SiCl_3^+$ are produced by direct, coupled mechanisms, while $SiCl_2^+$ is formed through an intimate collision involving a symmetric

intermediate. These mechanisms were interpreted in terms of the molecular orbital correlations. The cross section behavior and proposed mechanisms are consistent with those in our analogous study of the $Si^+ + SiF_4$ reaction.[39] Reaction thresholds were analyzed to derive the following thermochemical values: $\Delta_f H°_{298}(SiC\ell) = 44 \pm 6$ kcal/mol, $\Delta_f H°_{298}(SiC\ell^+) = 217 \pm 7$ kcal/mol, $IE(SiC\ell) = 7.44 \pm 0.40$ eV, and $\Delta_f H°_{298}(SiC\ell_2^+) = 188 \pm 3$ kcal/mol and 190 ± 6 kcal/mol.

In the second study, reactions of $SiC\ell_4$ with O_2^+, Ar^+, Ne^+, and He^+ were examined.[10] All reactions are fairly efficient with thermal energy rate constants that exceed 66% of the collision rate. The major products observed in the O_2^+ and Ar^+ reactions are $SiC\ell_4^+$ and $SiC\ell_3^+$, while for the Ne^+ and He^+ reactions, the major product is $SiC\ell^+$. Thermochemistry derived from these $SiC\ell_4$ systems includes the determination of $\Delta_f H°(SiC\ell_3^+) = 99.8 \pm 1.6$ kcal/mol and $\Delta_f H°(OSiC\ell_3^+) < 97$ kcal/mol from the O_2^+ system, and $\Delta_f H°(SiC\ell_2^+) = 184.9 \pm 2.6$ kcal/mol and $\Delta_f H°(SiC\ell^+) = 203.9 \pm 2.5$ kcal/mol from the Ar^+ system. We also derived the ionization energies: $IE(SiC\ell_3) = 7.65 \pm 0.15$ eV, $IE(SiC\ell_2) = 9.81 \pm 0.10$ eV, and $IE(SiC\ell) = 6.79 \pm 0.24$ eV.

In the third study, for which a manuscript is now being prepared for submission, we examined the reactions of $SiC\ell_n^+$ ($n = 1 - 3$) with $SiC\ell_4$.[22] Transfer of $C\ell^-$ and $C\ell$ between the neutral and ion reactant are the major reaction channels and are distinguished by silicon isotope labeling. For all systems investigated, transfer of $C\ell^-$ is the dominant channel. Also observed is simple collision-induced dissociation of the reactant ions by sequential loss of chlorine atoms.

G. Fluorocarbon chemistry

In several studies, we have examined reactions yielding ionized fluorocarbons. In one, dissociative charge transfer reactions of CF_4 with Ar^+, Ne^+, and He^+ were studied from thermal to 50 eV.[3] Only CF_n^+ ($n = 1 - 3$) products are observed in the reactions of Ar^+ and

Ne$^+$. In addition to the CF$_n$$^+$ products, both C$^+$ and F$^+$ are seen at high kinetic energies for the He$^+$ reactant. Reaction rates for these reactions were provided and compared with previous measurements. The energy dependences of the cross sections can be understood by considering the energies needed to access various states of the CF$_4$$^+$ ion.

This study led us to conclude that the thermochemistry of the CF$_3$$^+$ ion was not well established. In a second study, we performed a series of experiments designed to accurately determine the appearance energy of CF$_3$$^+$ from CF$_4$.[7] In contrast to a literature report,[44] there is no fluoride transfer equilibrium between CF$_3$$^+$ and SF$_5$$^+$. Thresholds for formation of CF$_3$$^+$ from reaction of ground state Kr$^+$(^{2}P$_{3/2}$) with CF$_4$ and from collision-induced dissociation of CF$_3$$^+$ by Xe are used to establish AE(CF$_3$$^+$/CF$_4$). Both results are in good agreement although the former experiment yields the most precise value, 14.24 $\pm$ 0.07 eV.

In a third study, the reactions of O$^+$ and O$_2$$^+$ with CF$_4$ and C$_2$F$_6$ were examined.[12] The predominant ions formed correspond to dissociative charge transfer reactions, with small amounts of FCO$^+$ and F$_2$CO$^+$ being formed. The thresholds and shapes of the dissociative charge transfer cross sections are explained in terms of vertical ionization to various electronic states of CF$_4$$^+$ and C$_2$F$_6$$^+$. In the O$^+$ reactions, fluoride transfer to form CF$_3$$^+$ + OF in the CF$_4$ system and C$_2$F$_5$$^+$ + OF in the C$_2$F$_6$ system is also observed at thermal energies. The formation of carbon oxyfluoride ions in these systems is postulated to occur by insertion of the oxygen ions into C-F bonds of the fluorocarbon molecules. From the O$_2$$^+$ + CF$_4$ and O$^+$ + C$_2$F$_6$ systems, Δ_fH$^\circ$(F$_2$CO$^+$) = 6.30 $\pm$ 0.08 eV is determined.

H. Reactions of atomic silicon ions with hydrocarbons

Several studies were designed to investigate the reactions of atomic ground state silicon ions with gasses potentially present in plasma systems. The first of these involved reactions with methane.[4] In this system, only endothermic processes are observed with

SiH^+ and SiH_3C^+ as the major ionic products. There is evidence that the latter species has two forms, Si^+-CH_3 formed at low energies, and a higher energy form that could be a triplet state of $SiCH_3^+$ or $HSiCH_2^+$. Minor ionic products include $SiCH_2^+$, CH_3^+, and $SiCH^+$. All observed products are consistent with a reaction that occurs via an $HSiCH_3^+$ intermediate. From the measured thresholds of the reactions and other information, the 298 K heats of formation (in kcal/mol) for the following silicon species are derived: $\Delta_f H°(SiH) = 91.4 \pm 1.8$; $\Delta_f H°(SiCH^+) = 339 \pm 7$; $\Delta_f H°(SiCH_2^+) = 285 \pm 3$; and $\Delta_f H°(SiCH_3^+) = 235 \pm 5$.

A comparable study on the reactions of $Si^+(^2P)$ with ethane (d_0, 1,1,1-d_3, and d_6) was later conducted.[13] At thermal energies, Si^+-CH_3 accounts for 90% of all products. Exothermic dehydrogenation to form $SiC_2H_4^+$ and demethanation to form $SiCH_2^+$ are observed, but these processes are inefficient. When CH_3CD_3 is employed as the reactant neutral, all products are observed to incorporate hydrogen and deuterium atoms in near-statistical distributions at low energies. This suggests that the primary HSi^+-CH_2CD_3, CH_3CD_2-SiD^+, and CH_3-Si^+-CD_3 intermediates are rapidly interconverted via a cyclic $HDSi(CH_2CD_2)^+$ intermediate.

In reactions of $Si^+(^2P)$ with methylsilane, SiH_3CH_3,[16] the major products at thermal energies are $SiCH_3^+$ and $Si_2HCH_3^+$, and above 1 eV, $SiH_2CH_3^+$. Labeling experiments involving $^{30}Si^+$ provide additional mechanistic information that $SiCH_3^+$ is formed via three different mechanisms. The general mechanistic details of this system can be understood by extending potential energy surfaces calculated elsewhere.[45] From the measured thresholds of the reactions and other information, we derived 298 K heats of formation (in kcal/mol) for the following disilicon ions: $\Delta_f H°(Si_2H_2CH_3^+) = 245 \pm 7$, $\Delta_f H°(Si_2HCH_3^+) < 290 \pm 2$, $\Delta_f H°(Si_2CH_3^+) = 258 \pm 2$, and $\Delta_f H°(Si_2CH_2^+) = 299 \pm 2$; the neutral silicon species: $\Delta_f H°(SiCH_3) = 79 \pm 7$, $\Delta_f H°(SiH_2CH_3) = 38.1 \pm 2.3$, and $\Delta_f H°[SiH_2(CH_3)_2] = -17 \pm 4$; and $\Delta_f H°(SiHCH_3^+) = 248 \pm 3$, and $\Delta_f H°(SiH_2CH_3^+) = 210 \pm 3$.

I.   Miscellaneous thermochemistry

Several studies were aimed at determining the thermochemistry of additional species of potential importance in plasma systems. One of these[5] involved measurements of the heat of formation of the hydroperoxyl radical, HO_2, and the ionization energy of methane, $IE(CH_4)$, both by studying the reaction of $O_2^+(^2\Pi_g$, v = 0) with CH_4. The thermodynamic values derived are $IE(CH_4)$ = 12.54 ± 0.07 eV, $\Delta_f H°_{298}(HO_2)$ = 3.8 ± 1.2 kcal/mol, $D_{298}°(H-OO)$ = 48.3 ± 1.2 kcal/mol, and $D_{298}°(H-OOH)$ = 88.4 ± 1.2 kcal/mol. In a more complete study of this reaction system,[8] we observed three previously reported reaction products, CH_2OOH^+, CH_3^+, and CH_4^+, as well as $CH_2O_2^+$, H_3O^+, and CO_2^+ at higher energies. Reactions of excited O_2^+ ions were also examined and are shown to be more efficient than those for ground state ions. The thermochemistry and potential energy surfaces for this reaction are discussed as well as the effects of vibrational, electronic, and translational energy on the reaction system. A heat of formation for $CH_2O_2^+$ of 201.5 ± 1.6 kcal/mol was measured and tentatively assigned to the methyne hydroperoxy ion structure, $HC-O-OH^+$.

Finally, a comprehensive study of the thermochemistry of sulfur fluoride cations and neutrals was performed.[17] By analyzing the energy dependences of the cross sections for CID of SF_n^+ (n = 1 - 5) with Xe, we obtained the following 0 K bond dissociation energies (BDEs): $D°(SF_4^+-F)$ = 4.60 ± 0.10 eV, $D°(SF_3^+-F)$ = 0.36 ± 0.05 eV, $D°(SF_2^+-F)$ = 4.54 ± 0.08 eV, $D°(SF^+-F)$ = 4.17 ± 0.10 eV, and $D°(S^+-F)$ = 3.56 ± 0.05 eV. The ionization energies, $IE(SF)$ = 10.16 ± 0.17 eV, $IE(SF_3)$ = 8.18 ± 0.07 eV, $IE(SF_4)$ = 11.69 ± 0.06 eV, and $IE(SF_5)$ = 9.60 ± 0.05 eV, were measured from analysis of endothermic charge-transfer reactions. From these BDEs and IEs, we derive heats of formation for the sulfur fluoride ions and neutrals that provide a self-consistent set of thermochemical data for the sulfur fluoride species, Table I.

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Table I. Heats of Formation (in kcal/mol) for SiF_n and SF_n Species at 0 K

species	$\Delta_f H°_0(X)$	species	$\Delta_f H°_0(X^+)$
SiF	-11.7 ± 2.1	SiF^+	$151.5(1.1)$
SiF_2	-152.2 ± 1.5	SiF_2^+	$96.7(1.2)$
SiF_3	-237.6 ± 1.1	SiF_3^+	$-29.4(0.6)$
		SiF_4^+	$-31.7(1.4)$
SF	8.3 ± 2.6	SF^+	240.9 ± 1.2
SF_2	-69.2 ± 2.8	SF_2^+	163.2 ± 2.6
SF_3	-111.6 ± 3.6	SF_3^+	77.0 ± 3.2
SF_4	-182.3 ± 3.7	SF_4^+	87.2 ± 3.4
SF_5	-221.8 ± 4.3	SF_5^+	-0.4 ± 4.1